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SEMIANNUAL PROGRESS REPORT
to the
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Grant NGR 33-010-101

Exobiology and the Origin of Life

March 15, 1971

CENTER FOR RADIOPHYSICS AND SPACE RESEARCH
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Summaries or citations of research supported by NASA Grant No. NGR 33-010-101 published or submitted to publication since the last semi-annual report are listed below:

- (1) Shock Synthesis of Amino Acids in Simulated Primitive Environments, Science, 168, 470-473, 1970.

A mixture of gases roughly simulating the primitive terrestrial atmosphere has been subjected to shock heating followed by a rapid thermal quench. Under strictly homogeneous conditions there is a very high efficiency of 5×10^{10} molecules per erg of shock-injected energy for production of alpha-amino acids. Calculations suggest that rapid quenching bypasses the usual thermochemical barrier. The product of energy flux and efficiency implies the unexpected conclusion that shocks occurring on atmospheric entry of cometary meteors and micrometeorites and from thunder may have been the principal energy sources for prebiological organic synthesis on the primitive earth.

- (2) Primordial Shock Synthesis of Amino Acids. Proceedings of the Third International Conference on the Origin of Life, Pont-a-Mousson, France, 1970 (R. Buvet and C. Ponnampereuma, eds.) North Holland Publishing Co., Amsterdam. [This is a more detailed version of the report cited in (1)].
- (3) Amino Acid Synthesis in Simulated Primitive Environments, Science, 170, 1001-1002, 1970.

The presence of ethane rather than methane, and assumptions on the flux of cometary meteors and micrometeorites used in previous work (Science, 168, 470, 1970), is shown to have no significant effect on the shock production of amino acids.

- (4) Long Wavelength Ultraviolet Photoproduction of Amino Acids on the Primitive Earth, submitted to Science.

Amino acids are produced under possible primitive Earth conditions by irradiation of gas mixtures with long wavelength ultraviolet light, representing the most abundant useful energy source for prebiological organic synthesis. H_2S is the initial photon acceptor in this work; superthermal H photodissociation products appear to initiate reactions leading to amino acid synthesis with an overall quantum yield $\sim 5 \times 10^{-5}$. (A preprint of this paper is included as Appendix III).

- (5) Synthesis of Cystine under Primitive Earth Conditions, submitted to Nature.

The disulfide cross-linkage of cystine plays a major role in the tertiary structure of proteins and in enzyme regulation and reaction kinetics. Long wavelength ultraviolet irradiation of primitive gases including H_2S yield cystine and cysteine, but no detectable methionine.

- (6) Production of Organic Molecules in the Interstellar Medium. Bulletin of the American Astronomical Society, 2, 340, 1970.

The presence of ammonia, water, formaldehyde, HCN, and (probably) methane in the interstellar medium, coupled with the known presence of shock waves, ultraviolet, cosmic ray, and other energy sources, strongly suggest that moderately complex organic compounds are a pervasive constituent of instellar matter. While an accurate simulation of interstellar conditions in the laboratory is entirely impractical, a range of previously published experiments indicate that a large array of aldehydes, hydrocarbons (including polycyclic aromatics), and other organic molecules is to be expected. The recent discovery of interstellar HCN is most important, because nitriles and aldehydes are known intermediates in the production of such organic molecules as amino acids and purines. In new experiments in which we attempt explicitly to simulate interstellar conditions, we find, produced stoichiometrically from ammonia and formaldehyde, the molecule hexamethylenetetramine, a very stable high melting-point ring compound which may be connected with interstellar grains. Ultraviolet irradiation of this molecule produces several compounds, of which HCN and C_2H_4 are most easily detected mass spectrometrically.

- (7) Detection of Several Non-Protein Amino Acids in the Presence of Protein Amino Acids, J. Chromatography, 54, 428-430, 1971.

Many non-protein as well as protein amino acids have been detected with the use of amino acid analyzers. However, there has been confusion as to whether these compounds are simultan-

ously distinguishable. We present evidence for separations of the following non-protein amino acids in the presence of their nearest protein amino acids: tryptophan, 3,5-diaminohexanoic acid, lysine, cis- Δ^4 -dehydrolysine, histidine, cysteic acid, urea, taurine, aspartic acid, methionine sulfone, hydroxyproline, threonine, glutamic acid, sarcosine, proline, α -amino-N-butyric acid, cystine, valine, betaine, methionine, L,L- α,ϵ -diaminopimelic acid, nor-valine, isoleucine, leucine, nor-leucine, tyrosine, phenylalanine, homocystine, and β -alanine. Data for 3,5-diaminohexanoic acid, cis- Δ^4 -dehydrolysine, and L,L- α,ϵ -diaminopimelic acid appear here for the first time.

- (8) Comments on Interstellar Organic Chemistry, in Proceedings of the IAU Discussion on Interstellar Molecules, in Transactions of the International Astronomical Union, 14 B, 1971, D. Reidel, Dordrecht, Holland, in press.

- (9) Experimental Jovian Photochemistry: Initial Results, submitted to Astrophysical Journal.

Experimental simulations of the ultraviolet photochemistry of the lower Jovian NH_4SH and NH_4OH clouds have been performed. With CH_4 , C_2H_6 , NH_3 , H_2S and H_2O as precursor materials the principal gas phase chemical and photochemical products are NH_4SH , $(\text{C}_2\text{H}_5\text{S})_2$, $(\text{C}_2\text{H}_5)_2\text{S}$, CH_3CN and possibly $(\text{CH}_3\text{S})_2$ and H_2S_2 . No trace of ammonium polysulfides is found under mass spectrometric analysis. The principal identified constituents in the NH_4OH solution are polymeric sulfur, S_1 through S_8 , and a range of

α -amino acids. An orange-brown polymeric material, reminiscent of the colors of the North Equatorial Belt, is produced. The NH_4OH clouds of Jupiter may be of considerable exobiological interest.

- (10) The Solar System Beyond Mars: An Exobiological Survey, Space Science Reviews, 11, 73-112, 1971.

An extensive discussion is presented on the organic chemical and exobiological potentialities of the exploration of the outer solar system. Optical and ultraviolet absorption features on Jupiter, the Jovian lower clouds, the Galilean satellites, Titan and the comets are of particular interest. Basic information relating to the origin of life on Earth and the possibility of extraterrestrial life may await the exploration of the outer solar system.

- (11) The Surface Environment and Possible Biology of Mars, in "Surfaces and Interiors of Planets and Satellites" A. Dollfus, ed., London, Academic Press, 1970, Chapter X, pp. 535-556.

Present knowledge and speculation on the habitability of Mars is reviewed critically and compared with the discussion in Alfred Russell Wallace's 1907 book, "Is Mars Habitable?" The comparison is sobering.

- (12) On the Origin of the Genetic Code, in "The Origins of Life" L. S. Margulis, ed., Gordon and Breach, 1971.

The manner in which a weakly stereospecific intrinsic genetic code, coding for only the active sites of primitive enzymes, could play a major role in the origin of life is explored.

(13) Life Beyond the Solar System, in "Exobiology" C.

Ponnamperuma, ed., North Holland Publishing Co., in press, 1971.

Related work, not supported by NASA, includes C. Sagan, "Life" 25,000 words, Encyclopaedia Britannica, 1970-1971 and subsequent editions; C. Sagan, The Origin of Life, in "Topics in the Study of Life", H. L. Roman and A. S. Sussman, eds., pp. 430-434, 1970, New York, Harper and Row; and N. H. Horowitz, F. D. Drake, S. L. Miller, L. E. Orgel and C. Sagan, The Origins of Life, Chapter 5 in "Biology and the Future of Man", P. Handler, ed., Oxford University Press, London, 1970, pp. 163-201.